THE COMPARATIVE TOLERANCES OF SOME FOULING ORGANISMS TO COPPER AND MERCURY *

CHARLES M. WEISS

Woods Hole Oceanographic Institution, Woods Hole, Massachusetts

The ability of marine organisms to attach to surfaces coated with ship-bottom paints depends on the toxicity of the surface and the sensitivity of the organisms to the toxic. Pyefinch (1946) presents a table showing the sensitivity of various organisms to toxics determined primarily from analysis of their settlement on toxic surfaces at Millport, Scotland. In the present studies carried out in the Biscayne Bay area, Florida, the tolerances of several common fouling organisms to copper and mercury have been compared by observations of the sequence of attachment to antifouling paints of moderate toxicity, to series of paints of graded toxicity, and to nontoxic surfaces adjacent to antifouling paint.

Results

An indication of the relative tolerance of various organisms to toxic paints can be obtained by observing the frequency of their attachments to paints which are beginning to fail after long exposure. It may be expected that the most tolerant forms will be the first to attach. The organisms attaching earliest to each of 662 antifouling paints exposed at Miami Beach and Tahiti Beach, Florida, were recorded with the following result:

Barnacles	67%
Encrusting bryozoans	18
Hydroids	9
Erect bryozoans	5
Tunicates	1
Tubeworms	< 0.1
Sponges	< 0.1

The order of attachment depends not only upon the tolerance of the organisms to the toxics, but also upon their seasonal occurrences. For example, hydroids and those forms following them in the list attach first only when barnacles and encrusting bryozoans are absent from the fouling population. Encrusting bryozoans rank below barnacles because they are absent during a large part of the year, while barnacles are present at almost all times. One of the encrusting bryozoans, *Watersipora cucullata*, appears to be somewhat more tolerant to copper than the most tol-

* Contribution No. 385 from the Woods Hole Oceanographic Institution. The observations described were made during an investigation of fouling by the Woods Hole Oceanographic Institution under contract with the Bureau of Ships, Navy Department, which has given permission for their publication. The opinions presented here are those of the author and do not necessarily reflect the official opinion of the Navy Department or naval service at large. The author is indebted to Dr. B. H. Ketchum and Dr. A. C. Redfield for helpful advice and criticism.

erant barnacle species, *Balanus amphitrite*, since it frequently attached earlier when both organisms were present.

The larva of a fouling organism which is unable to attach to a toxic paint surface may attach to a more resistant form which has already become established on the surface. Following this the adult may then spread over the paint surface. The relative tolerances of some fouling organisms to the toxic surfaces can frequently be assessed from these conditions of attachment.

The barnacles, *Balanus amphitrite* and *Balanus improvisus*, and the encrusting bryozoan, *Watersipora cucullata*, were found attached directly to paint surfaces. Attaching to and growing on these forms were *Schizoporella unicornis*, *Anomia* sp., *Bugula avicularia*, *Pennaria tiarella*, *Lepas anatifera* and tunicates. Examples of several of these organisms which were unable to attach to antifouling paints, but which attached to other forms on the paint, are shown in Figures 1–5.

A more precise evaluation of tolerance is given by comparing the frequency of attachment of different organisms on a surface of moderate toxicity with their frequency on a nontoxic control surface. A paint of moderate toxicity will allow attachment only of the forms having the highest tolerance to the paint toxics. Glass panels coated on one side with a paint in which cuprous oxide served as the toxic were exposed for periods of one month. The uncoated side served as a control. The use of the glass panel gave both surfaces the same color, thus eliminating any differential effect of color on attachment. Table I shows the numbers of barnacles

TABLE I

Total number of barnacles attached to 33 nontoxic and toxic surfaces (80 square inches in area) exposed for one month at intervals between October 1944 and May 1946

Barnacle species	Barnacles on nontoxic surface		Barnacles on toxic surface	
	Total	% of total	Total	% of total
Balanus improvisus	17,959	89.7	15	9.4
Balanus amphitrite	1,503	7.5	145	90.6
Balanus eburneus	564	2.8	0	0.0

of three species collected on these two surfaces. The total numbers of barnacles attaching to the toxic paint surface are less than one per cent of those growing on the nontoxic control. *Balanus amphitrite* comprises over 90 per cent of the population on the toxic surface, being the only barnacle species on most panels, though it is only 7.5 per cent of the population attaching to the control surface. In contrast *Balanus improvisus* makes up 90 per cent of the total attachment to the nontoxic surface but comprises only 9.4 per cent of the population on the paint. *Balanus eburneus* is completely inhibited from the toxic surface. It is thus evident that each of these three species of the same genus demonstrates a different degree of tolerance to the copper paint.

In addition to the barnacle fouling the only other significant attachment to this paint surface was the encrusting bryozoan *Watersipora cucullata* and the green alga *Enteromorpha* sp. Both of these species attached only during the periods of their maximum abundance. On the nontoxic panels a total of twenty species of fouling

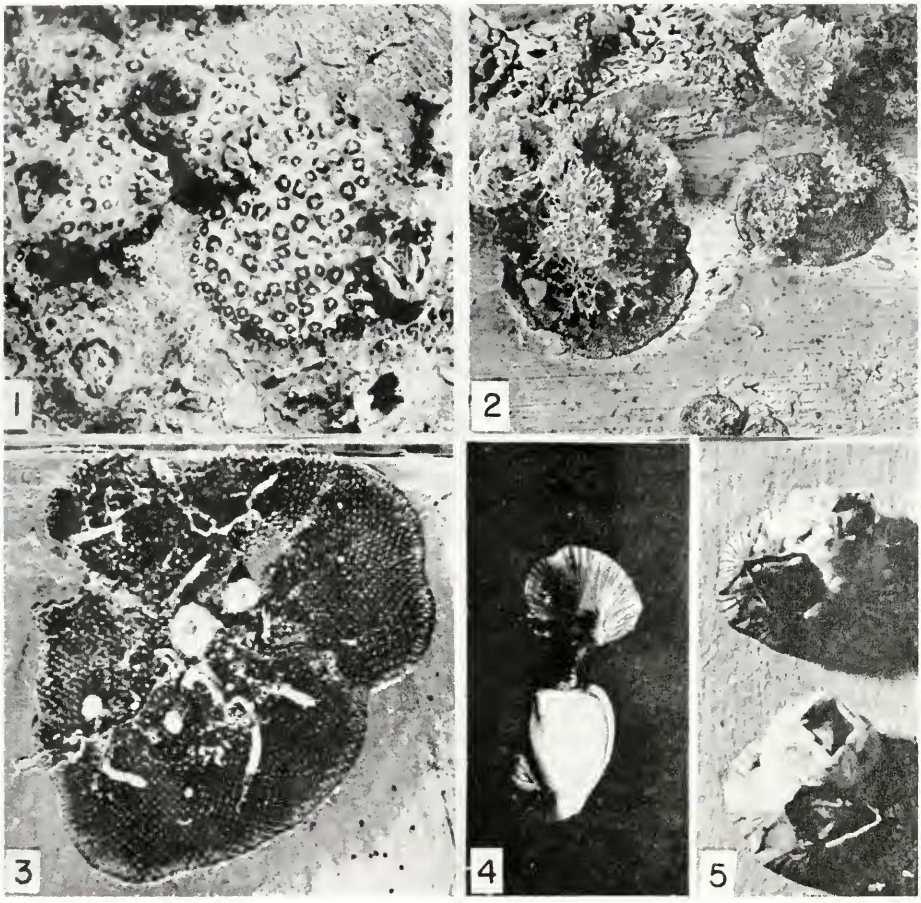

PLATE I

FIGURE 1. A speckled tunicate limited in attachment to barnacles and *Anomia* sp. without spreading onto the paint surface.

FIGURE 2. *Bugula avicularia* attached to the encrusting bryozoan, *Watersipora cucullata*, which is growing directly on the paint.

FIGURE 3. Barnacles attached to *Watersipora cucullata* which developed directly on the paint surface. Tubes of *Dasychone conspersa* are also attached on *W. cucullata*.

FIGURE 4. Gooseneck barnacle, *Lepas anatifera*, attached to *Balanus amphitrite* which attached to an otherwise effective antifouling paint on a ship's bottom.

FIGURE 5. Two examples of *Balanus improvisus* which attached to the more resistant barnacle, *B. amphitrite*. Photographed after removal from the paint surface.

organisms attached during the period covered by these observations. These must be considered to be less tolerant than the four organisms which attached to the paint surface.

In order to establish the relative tolerances to copper of the more sensitive fouling forms a set of paints containing graded amounts of copper flake pigment was prepared. The copper leaching rates of these paints were measured as described by

Ketchum, Ferry, Redfield, and Burns (1945) and were found to vary in proportion to the pigment content and to decrease with the time of exposure. This series thus provided graded toxicities.

The relative tolerance of attaching organisms could be judged by the time of exposure elapsing before they attached to any one member of the series or by the number of members of the series which were fouled at any one time. The paints were applied to 8 × 10-inch weldwood panels which were immersed at Miami Beach and Tahiti Beach, Florida. The composition of the paints and the time of exposure before various fouling forms attached are given in Table II.

TABLE II

Number of months of exposure prior to appearance of fouling on painted panels immersed in the sea at Miami Beach, Florida (May 2, 1945–March 2, 1946), and at Tahiti Beach, Florida (May 2, 1945–September 2, 1945). The paints contained graded amounts of copper flake in a vehicle consisting of equal parts, by weight, of polyvinyl butyral and rosin.

Paint number Copper content, per cent dry weight	AF12 90	121 67	122 45	123 30	124 23	125 14
Miami Beach						
Balanus amphitrite	4	3	3	2	1	1
Watersipora cucullata	9	9	8	2	2	1
Balanus improvisus	a	a	a	a	2	1
Tahiti Beach						
Polysiphonia sp.	3	2	2	2	2	2
Balanus amphitrite	b	b	4	4	3	1
Hydroides parvus	b	b	b	4	4	3

a. None of this species had attached to these paints after 10 months of exposure.
b. None of these species had attached to these paints after 4 months of exposure.

At Miami Beach only three fouling organisms attached to the copper paints, two species of barnacles and the encrusting bryozoan *Watersipora cucullata*. Throughout the period of exposure there was no marked seasonal variation in the incidence of barnacles. However, seasonal fluctuation in the incidence of *Watersipora cucullata* accounts principally for the nonattachment of this organism between the second and ninth months of immersion of the paints. Its absence from the paints is, therefore, not indicative of its sensitivity to the paint toxic.

The exposure at Tahiti Beach, Florida, indicated that, on these copper paints, a red alga of the genus *Polysiphonia* is more tolerant, and that the tube worm, *Hydroides parvus*, is less tolerant than *Balanus amphitrite*.

Some species of fouling were too sensitive to attach even to the paints of lowest toxicity. To ascertain their relative tolerance of paint toxics their sequence of attachment was noted on nontoxic areas adjacent to paint surfaces. Observations by Miller (1946) on the diffusion of toxics from antifouling paints indicate that toxic gradients exist, decreasing from the paint edge. To provide nontoxic areas for attachment adjacent to the paint surfaces, strips 5, 10, and 20 mm. in width were left free of paint on the panels of the graded toxicity series.

At both exposure locations colonial tunicates attached to the widest bare strips on the paints of lowest toxicity, AF124 and AF125, by the second month of immersion.

By the third and fourth months of exposure hydroids had attached to the initial fouling on these nontoxic areas. These observations indicate that tunicates are more tolerant than hydroids to copper but less tolerant than those forms able to attach directly to the paint surface.

From the preceding observations several fouling forms can be arranged in order of decreasing tolerance to copper as follows: *Polysiphonia* sp., *Watersipora cucullata*, *Balanus amphitrite*, *Balanus improvisus*, *Balanus eburneus*, *Hydroides parvus*, tunicates and hydroids.

In the examination of antifouling paints employing mercury pigments or mixtures of mercury and copper pigments as the toxic ingredients, it was noted that certain of the fouling organisms appeared to be more sensitive to mercury than to copper while for others the reverse was true.

To establish the comparative tolerance of different species to mercury a series of paints containing mercurous chloride in graded concentration was made. The vehicle was the same as that used for the copper series. The mercury content of these paints was equal in weight to the corresponding member of the copper series. These paints were immersed simultaneously and at the same locations as the copper paints. The extent of exposure before fouling attached to the paint surfaces of the AF12 mercury series is shown in Table III.

Table III

Number of months of exposure prior to appearance of fouling on painted panels immersed in the sea at Miami Beach, Florida (May 2, 1945–March 2, 1946), and at Tahiti Beach, Florida (May 2, 1945–September 2, 1945). The paints contained graded amounts of mercury, added as mercurous chloride, in the vehicle described in Table II.

Paint number Mercury content, per cent dry weight	AF12 90	121 67	122 45	123 30	124 23	125 11
Miami Beach						
Balanus amphitrite	9	9	2	2	2	1
Balanus improvisus	a	a	a	4	9	2
Bugula neritina	a	a	a	2	6	1
Watersipora cucullata	a	a	a	6*	a	4*
Tahiti Beach						
Polysiphonia sp.	b	b	b	3	3	1
Balanus amphitrite	b	b	b	b	2	2

a. None of these species had attached to these paints after 10 months of exposure.
b. None of these species had attached to these paints after 4 months of exposure.
* Single specimen not present on following month.

At Miami Beach four organisms attached to this series of paints. The most resistant of these was *Balanus amphitrite*, followed in order by *B. improvisus* and *Bugula neritina*. *Watersipora cucullata*, which was found to be quite tolerant of copper, attached to only two of these paints, and in neither case was the attachment secure. In contrast, *Bulgula neritina* was able to attach directly to the mercury paints but was never found on any of the comparable copper paint surfaces. At Tahiti Beach *Polysiphonia* sp. was found to be more tolerant than *Balanus amphitrite* to the mercury paints.

Photographs of two of the copper and two of the mercury paints of these series, after nine months of exposure at Miami Beach, are shown in Figure 6. The ability of *Watersipora cucullata* to attach to the copper paints and its absence from the comparable mercury paints are shown. Both of the copper paints and one of the mercury paints are fouled with *Balanus amphitrite*.

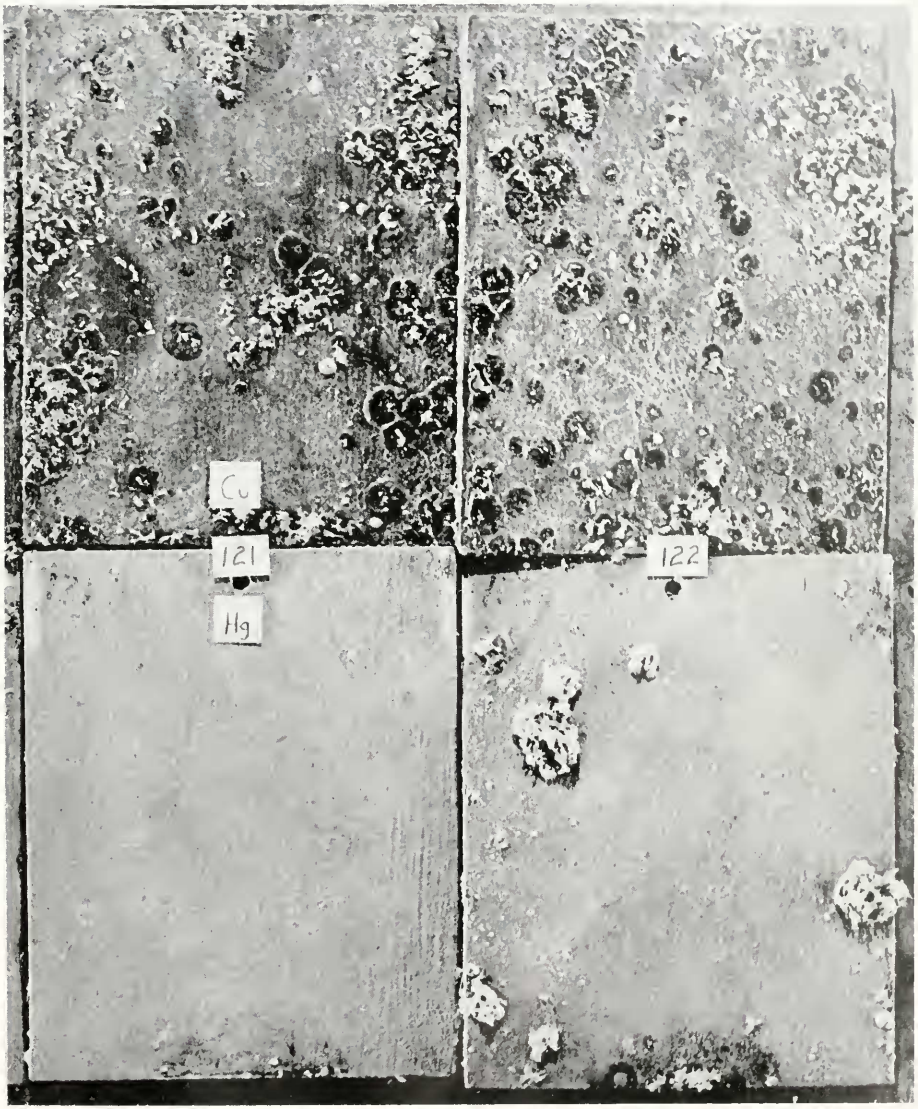

PLATE II

FIGURE 6. Comparison of the attachment of *Watersipora cucullata* to paints pigmented with copper and mercury after nine months of exposure. *W. cucullata* appears on the copper series (top panels) as the dark disc-like organisms.

Nontoxic strips on panels otherwise coated with the mercury paints permitted attachment of the more sensitive fouling forms. The more resistant forms mentioned above always attached first to these nontoxic areas. In addition, *Watersipora cucullata*, *Anomia* sp., hydroids and tunicates invaded the unpainted areas at Miami Beach. At Tahiti Beach *Enteromorpha* sp. and *Hydroides parvus* attached in the order given.

These exposures indicate the following order of decreasing tolerance of some fouling organisms to mercury as a paint toxic: *Polysiphonia* sp., *Balanus amphitrite*, *Bugula neritina*, *Balanus improvisus*, *Watersipora cucullata*, *Anomia* sp., *Enteromorpha* sp., *Hydroides parvus*, hydroids and tunicates.

From the results of the various methods described above the comparative tolerance of several fouling organisms to copper and mercury has been evaluated. The results are given in Table IV. The organisms listed as attaching to adjacent

Table IV

The comparative tolerance of some fouling organisms of the Biscayne Bay area, Florida, to copper and mercury employed as pigments in antifouling paints. The lists are arranged in approximate order of decreasing tolerance.

	Copper	Mercury
Organisms found attached to toxic paint surfaces	*Polysiphonia* sp. *Watersipora cucullata* *Balanus amphitrite* *Enteromorpha* sp. *Balanus improvisus* *Balanus eburneus* *Hydroides parvus*	*Polysiphonia* sp. *Balanus amphitrite* *Bugula neritina* *Balanus improvisus* *Watersipora cucullata*
Organisms found mainly attached to nontoxic areas adjacent to paint surfaces	*Anomia* sp. *Bugula neritina* *Bugula avicularia* *Lepas anatifera* tunicates hydroids	*Anomia* sp. *Enteromorpha* sp. *Hydroides parvus* hydroids tunicates

nontoxic surfaces include those which may on occasion be found on paints of low toxicity but which generally do not attach directly to the paint surface. The exact position in the order of decreasing tolerance, for all but the first three organisms in each column, requires further verification.

Discussion

Relatively few of the sessile species in the Miami area which attach to neutral surfaces are able to attach to antifouling paints. Even paints of such low toxicity that they become completely covered permit the attachment of only four or five forms. Many less resistant fouling organisms are excluded from the paint surface. Effective antifouling paints must be designed to prevent the attachment of the few most tolerant forms.

The species most tolerant of copper are different from those most resistant to mercury. The conflicting opinions which have existed concerning the relative

efficiencies of copper and mercury compounds as paint toxics may depend largely on the species of fouling organisms present at the particular testing location.

The present results and those given by Pyefinch (1946) agree in showing that *Enteromorpha* and *Polysiphonia* are among the more resistant forms, and *Anomia* and tunicates have low tolerance to paint toxics. Tubularian hydroids were noted only as secondary fouling at Miami, though Pyefinch rates them more resistant than *Balanus* and equal to *Enteromorpha*. A direct comparison of the results with *Balanus* is not feasible since the three species found in Miami showed marked differences in toxic sensitivity. None of these species are found at Millport where Pyefinch's studies were made. Pyefinch lists a greater variety of algae, including diatoms, which were not included in the investigations at Miami.

Summary

The comparative toxic tolerance of several fouling organisms was based on the sequence of their attachment to copper and mercury antifouling paints. A red alga, *Polysiphonia* sp., and the barnacle, *Balanus amphitrite,* were the most tolerant and attached to copper and mercury paints before other organisms. The encrusting bryozoan, *Watersipora cucullata,* was found to be slightly more tolerant to copper but considerably less tolerant to mercury than the above two forms. Less tolerant forms were *Balanus improvisus, Hydroides parvus, Bugula neritina, Anomia* sp., *Enteromorpha* sp., tunicates and hydroids. Other species, though attaching to nontoxic surfaces, were never found on the toxic paints.

LITERATURE CITED

Ketchum, Bostwick, H., J. D. Ferry, A. C. Redfield, and A. E. Burns, Jr., 1945. Evaluation of antifouling paints by leaching rate determination. *Ind. Eng. Chem.*, **37**: 456–460.

Miller, Milton A., 1946. Toxic effects of copper on attachment and growth of Bugula neritina. *Biol. Bull.,* **90** (2) : 122–140.

Pyefinch, K. A., 1946. Methods of assessment of antifouling compositions. *Jour. Iron and Steel Inst.,* 1945, No. II, pp. 229–243.